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Nanofiltration for dextrose recovery from crystallization mother liquors: A feasibility study

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ABSTRACT

A wide experimentation was carried out to test performances of industrial NF modules for dextrose (DX) recovery from crystallization mother liquors, coming from dextrose manufacturing by saccharification of starch hydrolizates. Real solutions were processed containing total Dry Substance (DS) in the range from 17 to 43 wt% and DX content close to 80–83%; impurities being mainly maltose and other sugars with higher degree of polymerization.

Aim of the work was to achieve at least a DX purity of 95% in correspondence with average transmembrane fluxes higher than 4 $dm^3/(hm^2)$.

Four commercial spiral wound modules with polyamide membranes were tested, manufactured by KOCH-Membrane Systems and by GE Power&Water (well-known as DESAL membrane products). Module performances were measured at temperatures from 30 to 50 °C, at pressures from 15 to 30 bar.

Nanofiltration is confirmed as a feasible technique to get preferential permeation of dextrose.

For all the modules tested many analogies were observed in their behavior as a function of operative conditions. In spite of the complexity of the solutions investigated, module performances can be easily described by using few simple quantities (DS wt%, DX purity, total flux, DX rejection and Impurities Rejection). DX purity in the Permeate is strictly dependent on the DX purity in the module feed and on the total volume flux.

Results give a general indication about the experimentation protocol to be performed in order to obtain basic data useful both to test the process feasibility and to scale-up the process.

Membranes tested showed different separation efficiencies; only the module GE-DL4040C1025 fitted the industrial requirements for the process application. Modules GE-DL can be used with confidence at 50 °C and 30 bar, in a range of feed flow rates from 2300 to 3600 L/h, achieving DX purity in the Permeate higher than 97%; correspondingly, the NF plant can be designed to work with a DS content in the feed stream from 22 wt% to 35 wt%, obtaining total fluxes from 16 to 6 $dm^3/(hm^2)$ and a DS content in the Permeate from 11.5 wt% to 22.5 wt%, correspondingly.

1. Introduction

Production of high purity monosaccharides is of great interest for food and pharmaceutical industry.

Dextrose is typically produced on industrial scale by saccharification of starch hydrolyzates; after saccharification, dextrose with a purity above 90% is usually recovered by crystallization in the form of crystallized dextrose. The by-product of the crystallization process, the mother liquor, is generally sold to the food industry as a low quality syrup. Unfortunately, the syrup is produced at relatively high amounts which negatively affect the efficiency of the overall dextrose production process, since they are sold under cost.

The industry requirement is then the development of an economically-competitive process to increase the yield of the current dextrose production processes with a twofold purpose: decreasing the amount of by-products and enhancing their quality to achieve a commercially attractive purity in dextrose.

The mother liquor usually comprises any starch hydrolysis product other than dextrose such as disaccharides, trisaccharides and oligosaccharides; it is typically available at pH conditions in the range from 3.5 to 4.5 and it is warmly recommended to be processed at temperatures higher than 40 °C, preferably at 50 °C

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List of symbols

DS	Dry Substance
DX	dextrose
IMP	impurities (IMP = DS − DX)
F	stream out of the tank (defined in Fig. 2)
F1	stream into the module (defined in Fig. 2)
R	Retentate back to the tank (defined in Fig. 2)
R1	Retentate out of the module (defined in Fig. 2)
RR	partial recirculation of Retentate (defined in Fig. 2)
P	Permeate out of the module (defined in Fig. 2)
A_m	module area
C	mass concentration (kg/m^3)
Jv	total volume flux (dm^3/(hm^2))
Q	volume flow rate (m^3/h)
pur	purity (wt% on DS); ex: pur^P_{DX} = DX purity in the Permeate
R^{obs}	observed rejection
ω	weight%; ex: ω^{F1}_{DS} = weight% of DS in F1

in order to inhibit fermentation. Dextrose purity of the mother liquor is typically in the range from 78% to 83% on the total Dry Substance. The main requirement is to increase dextrose purity to an extent higher than 95%, so that the stream can be recirculated to the main production line. The target of 95% purity is a tight specification constrained by the overall process; the highest content as possible of total Dry Substance is appreciated also.

Chromatographic techniques [1–4] are generally applied with interesting efficiencies to the separation of isomers (fructose from glucose, for instance) as well as to the purification of monosaccharides with different carbon number (pentoses from hexoses, and so on) and finally to the separation of oligosaccharides (raffinose from sucrose, for instance).

On the other hand, Nanofiltration membranes typically show molecular weight cut-offs in the range from 200 to 1000 Da. Data from technical sheets generally report almost complete retention of neutral solutes such as simple sugars, making reference to tests performed with aqueous solutions containing single solutes at low concentration. As far as sugar solutions is concerned, NF can be certainly proposed for the concentration of aqueous solutions containing polysaccharides, as a preliminary step before conventional evaporation, for instance. However, many studies and a wide experimentation document the applicability of Nanofiltration for the separation of monosaccharides from disaccharides and oligosaccharides [5–13], for the separation of xylose from glucose [14,15], for the purification of disaccharides and other mixtures [16–21]. Most of the applications proposed use polymeric membranes (generally polyamide or cellulose acetate); some authors tested also ceramic membranes and introduced a process by integration of ultrafiltration with a Nanofiltration step [22].

In spite of the relatively low differences among the molar mass of monosaccharides and di-/tri-saccharides, separation by NF occurs with interesting yields for glucose from sucrose, as well as for glucose from lactose, or from raffinose, and so on. Most of the published results refer to experiments with small flat membranes samples, generally in plate and frame cells, addressed to demonstrate the primary feasibility of the process and to put in evidence the role of the main operative parameters. Tests were generally performed at room temperature in a total concentration range typically lower than 50 g/L; only in some cases authors carried out experimentation at higher compositions (100–300 g/L) [14,21] or at temperatures close to 50 °C [13–15].

Finally, it can be observed that only in few cases performances of commercial modules were tested; as an example Feng et al. [13] and Zhang et al. [16] tested small spiral wound modules.

On the other hand, the interest of food industry for Nanofiltration of sugar solutions is well documented by a wide patent production [23–33].

Patent [23] claims the possibility to use a Nanofilter to treat a glucose syrup containing 95% dextrose and 5% di-trisaccharides obtaining a Permeate with dextrose purity in a range well over 99%.

Patents [24,25] are remarkable. They describe a process for the manufacture of a starch hydrolysate with high dextrose content in which various membrane opportunities are introduced; in particular, authors integrate microfiltration with Nanofiltration to recover enzymes and a Permeate with a high dextrose purity, in order to improve the main production line of dextrose.

In patent [26] the invention relates to a Nanofiltration process integrated with an enzymatic treatment applied to by-products of the main production line of dextrose in order to increase the overall yield of dextrose.

The recovery of disaccharides from oligosaccharides, such as purification of sucrose from invert sugars [27] and maltose from maltotriose [28] is also introduced.

Finally, NF is widely applied to the separation of xylose from glucose [29–31] and to the development of Nanofiltration processes, for the separation and recovery of sugars at low molecular weight from polysaccharides [32,33]. Various configurations are proposed of Nanofiltration stages in which the Retentate and Permeate streams can be recycled to previous stages, by designing a flow pattern typical of a fractionated unit operations; integration of the membrane process with a chromatographic separation is also proposed.

It is self-evident that Nanofiltration can be used advantageously in the separation of dextrose from polisaccharides at various molecular weights. However none of the papers introduce any criterions for the selection of membranes suitable for the process, neither document which experimental data can be necessary to scale up the process and to design the corresponding plant on an industrial scale.

This paper is then addressed to test the applicability of Nanofiltration to the purification of dextrose from industrial solutions containing polisaccharides at different degrees of polymerization, assuming as primary target to achieve a dextrose purity higher than 95%, starting from dextrose purity close to 80%. The characterization of commercial spiral wound modules performances and the definition of the best operative conditions for the process development are the main objects of the project. A general indication of the basic experimental data useful for the process scale-up is obtained and correspondingly a criterion for the selection of the most performing membranes is suggested straightforwardly.

2. Materials and methods

2.1. Solutions

Industrial real solutions were tested; samples were taken from the by-product streams of the crystallization process downstream saccharification steps, after demineralization treatments.

Real solutions contain Dry Substance (DS) in the range from 45 to 55 wt%, given by monosaccharides (with molar mass equal to 180 kg/kmol), mainly dextrose (DX), and oligosaccharides at various degrees of polymerization (with molar mass equal/greater

than 342 kg/kmol), mainly maltose with low content of maltotriose and greater oligosaccharides.

Although very complex, for the aim of the experimental investigation, solutions can be modeled as ternary mixtures containing water, dextrose and impurities. Typically, average values of DX purity in the tested solutions were in the range from 80 to 83 wt% calculated on the total DS; conductivity was measured lower than 5 microS/cm at room temperature. During the experimentation, pH was kept in the range from 3.8 to 4.5, which corresponds to the typical pH conditions existing in the plant.

Because of the chemical nature of the solutions, chemical–physical properties necessary for data elaboration were calculated by using literature data [34], assuming the solutions as DX-water solutions at the composition corresponding to the DS% content.

2.2. Membranes and Nanofiltration apparatus

Four commercial spiral wound modules with polyamide membranes were tested in this project, manufactured by KOCH-Membrane Systems and by GE Power&Water (well-known as DESAL membrane products), respectively KOCH-4720SR2-N1 and KOCH-MPS34A2Z, GE-DK4040C1027 and GE-DL4040C1025. Geometrical details, abbreviations, nominal rejections as well as hydraulic permeabilities are listed in Table 1; each module was 4 in. nominal diameter, 40 in. nominal length and designed for food applications. Hydraulic permeabilities were calculated by data reported in technical sheets [35,36], according to the typical equations of the solution–diffusion model [37], in correspondence with the same conditions.

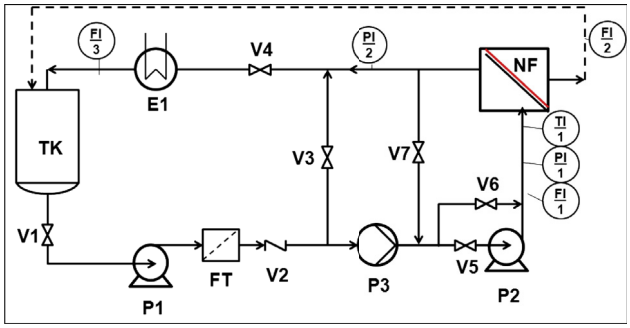
Modules were tested in a pilot plant, represented by the simplified flow sheet reported in Fig. 1.

The set-up was designed to work both in batch operation mode and in continuous operation mode. It was used in batch operation mode with different configurations (Fig. 2): (a) in total recirculation mode of Retentate (Fig. 1; valves V5 and V7 closed – V6 open); (b) in partial recirculation mode of Retentate (Fig. 1; valves V5 and V7 open – V6 closed) in order to allow high feed flow rates in the stream F1. In configurations (a) and (b) the Permeate stream P was continuously withdrawn out of the plant, thus giving a continuous concentration of the tank solution. The plant in configuration (b) was used to perform long time trials also, in which the Permeate was completely recirculated back to the tank in order to keep constant conditions during experimentation.

2.3. Experimental procedure

2.3.1. Start-up

A protocol was defined for the start-up of a virgin module. The same procedure was followed every time a module was installed in the NF equipment, after a period of inactivity in a storage solution (typically sodium metabisulfite 0.5 wt%); in that case the module was firstly rinsed with de-ionized water in a single-pass plant configuration, at room temperature, to eliminate the storage solution.



Equipment list		Instruments	
TK	Tank	V1, V3,V5,V6,V7	Regulating valves
FT	Cartridge filter	V2	Check valve
P1, P2	Centrifugal Pump	V4	Needle valve
P3	Positive displacement pump	PI	manometer
E1	Heat exchanger	TI	Thermometer
NF	Nanofiltration module	FI	Flow meter

Fig. 1. Experimental set-up.

The start-up procedure consists in three subsequent steps.

2.3.1.1. Stabilization. It is performed with demi-water in the plant configuration (b) with total recirculation of Permeate (Fig. 2) at 10 bar inlet pressure, at pH = 4 in the tank, at 30 °C for 2–3 h and then at 50 °C for 1–2 h; volume flow rate in F1 was set at 3.5 m^3/h. Stabilization is assumed completed when Permeate flow rate is measured as a constant value vs. time in a range of 30–45 min.

2.3.1.2. Washing procedure. It is performed in the plant configuration (b) with total recirculation of Permeate (Fig. 2). A basic cleaning step (aqueous solution of KOCHKLEEN® at pH = 11, 40 °C, 3 bar inlet pressure, at 3.5 m^3/h volume flow rate in F1, for 1 h long) is alternate with an acid cleaning step (aqueous solution of HNO_3 at pH = 4, room temperature, 3 bar inlet pressure, at 3.5 m^3/h volume flow rate in F1, for 1 h long). Each cleaning procedure is followed by a rinse step with de-ionized water performed in a single-pass plant configuration, at room temperature, at 3.5 m^3/h volume flow rate in F1, at 3 bar inlet pressure for 30 min and then 10 bar inlet pressure for 30 min; rinsing is concluded when pH values of Permeate and Retentate correspond to the feed pH.

2.3.1.3. Water flux measurements. Measurements of total flux across the modules are performed with demineralized water at 50 °C and

Table 1
Spiral wound modules: geometrical characteristics and performances (data from technical sheets [35,36]).

Model & abbreviation	DK4040C1027 GE-DK	DL4040C1025 GE-DL	4720SR2-N1 K-SR2	SelRO MPS-34A2Z K-MPS34
Manufacturer	GE Power&Water		KOCH Membrane Systems	
NaCl retention @ conditions	n.a.	n.a.	30% @ 2 g/L, 3.8 bar, 25 °C	35% @ 50 g/L, 30 bar, 30 °C
$MgSO_4$ retention	98%	96%	95%	n.a.
Permeate flow (m^3/d)	7.6	6.0	11.7	5.8
Recovery @ conditions	15% @ 2 g/L, 7.6 bar, 25 °C	15%	15% @ 5 g/L, 6.6 bar, 25 °C	pure water, 30 bar, 30 °C 97%/95%
Sucrose/glucose retention @ conditions	n.a.	n.a.	n.a.	@ 30 g/L, 30 bar, 30 °C
Active area (m^2)	9.1	6.1	7.3	4.0
Feed spacer (mil)	30	50	31	57
Hydraulic permeability ($dm^3\ h^{-1}\ m^{-2}\ bar^{-1}$)[a]	5.1 @ 25 °C	6.0 @ 25 °C	14.3 @ 25 °C	2.0 @ 30 °C

[a] Calculated according to solution–diffusion model [37].

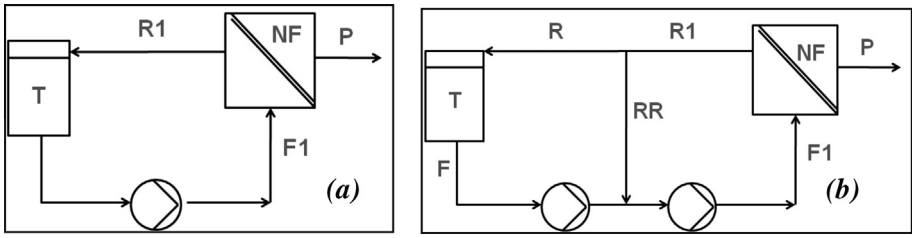


Fig. 2. Configurations for batch operation mode: (a) total recirculation mode of Retentate; (b) partial recirculation mode of Retentate.

pH = 4 in a pressure range from 3 to 12 bar at the feed side; hydraulic permeability of the membrane can be calculated straightforwardly, both for the washed virgin membrane and after permeation of sugar solutions. The corresponding value for the cleaned virgin membrane is assumed as a reference value to check if the membrane performances change during NF operations: a decrease in permeability is frequently observed after NF experiments, with respect to the value obtained with the cleaned virgin membrane. A washing procedure step is run when a decrease higher than 20% is observed in the hydraulic permeability; during experimentation, original performances of the cleaned membrane were generally obtained after a complete washing cycle, thus indicating that the washing procedure was successful.

As an example, hydraulic permeabilities of the cleaned membranes were measured as 6.0 and 8.6 $dm^3/(hm^2\ bar)$ at 30 °C for GE-DK and GE-DL modules respectively, and 6.4 $dm^3/(hm^2\ bar)$ at 50 °C for K-MPS34. It can be observed that they are in good agreement with the same values reported in Table 1, accounting that permeabilities should obviously increase with temperature.

2.3.2. Filtration experiments and sample analysis

All the experiments were performed by controlling temperature, pressure and volume flow rate in stream F1, as well as the pH in the tank (see Figs. 1 and 2); volume flow rates in streams P and R were measured straightforwardly as a function of time and, contemporary, samples were taken of the solutions in the tank, in the Permeate P and in the Retentate R.

For each sample, total Dry Substance was measured as DS wt% by a refractometer; sugars compositions were measured by an HPLC system equipped with a sugar column Aminex in calcium form followed by an RI detector, according to the standard procedure defined in the laboratories at the plant of Castelmassa (RO-Italy) (oven at 85 °C, detector at 35 °C, HPLC grade water at 0.6 mL/min as mobile phase, 68 bar maximum pressure).

NF experiments were performed with diluted real solutions in the range from 17 to 43 wt% of DS; demineralized water was used for dilutions.

3. Module performances: Results and discussion

A detailed report is given of the results obtained in all the experiments performed with NF modules, whose properties are shown in Table 1. Notation used in this section is reported in the List of symbols.

As discussed in the Introduction, aim of the work was to test the capability of a NF process to achieve at least a DX purity of 95% in correspondence with acceptable transmembrane fluxes, starting from real solutions with a DX purity in the range from 80% to 83%; average fluxes higher than 4 $dm^3/(hm^2)$ are recommended.

All the results obtained with different modules have been organized in order to draw a general trend of module performances, according to the criterion explained in the following section.

3.1. Parameters and data reduction

3.1.1. Stream modeling

The real system is modeled as a ternary mixture containing water (described by the Dry Substance – *DS wt%*), Dextrose (described by the DX purity which leads to the DX composition) and Impurities (*IMP*), assumed as the complement of DX to DS. In the specific case under investigation, Impurities are mainly maltose.

3.1.2. Module parameters and relevant quantities

Since not very high fluxes across the modules were measured with sugar solutions, it was self-evident that module performances could be described by using average properties which refer to the conditions existing at the inlet section of the module itself.

In addition, the whole experimentation put in evidence that it was possible to characterize the module by using few relevant quantities, such as the average total volume flux across the module (Jv), the average observed rejections of DX (R_{DX}^{obs}) and of Impurities (R_{IMP}^{obs}), the DS composition (DS wt%), the DX purity in Permeate and in Retentate.

Such quantities were observed to be interdependent each other as indicated in relationships from Eqs. (1)–(4) (notation makes reference to Fig. 2 and to the List of symbols). In particular, when the pressure was set in the module feed (stream F1), the average total volume flux as well as DS% in Permeate were measured simply dependent on DS wt% in the module feed and generally independent of DX purity, in the purity range investigated. Correspondingly, observed rejections showed to be mainly a function of the total flux. Synthetically, we observed that:

$$Jv = \frac{Q_P}{A_m} = f(\omega_{DS}^{F1});\ \omega_{DS}^{P} = f(\omega_{DS}^{F1}) \tag{1}$$

$$R_{DX}^{obs} = 1 - \frac{C_{DX}^{P}}{C_{DX}^{F1}} = f(Jv);\ R_{IMP}^{obs} = 1 - \frac{C_{IMP}^{P}}{C_{IMP}^{F1}} = f(Jv) \tag{2}$$

in which ω_{DS}^{F1} represents weight% of DS in F1.

With reference to the DX purity in Permeate, by its definition we can simply obtain the following relationships:

$$pur_{DX}^{P} = \frac{C_{DX}^{P}}{C_{DX}^{P} + C_{IMP}^{P}} = \frac{\alpha}{1+\alpha};\ \alpha = \frac{C_{DX}^{F1}}{C_{IMP}^{F1}} \frac{1 - R_{DX}^{obs}}{1 - R_{IMP}^{obs}} \tag{3}$$

in which we can observe that DX purity in Permeate is generally dependent on the observed rejections and on the DX purity in the feed. As a consequence, by coupling relationships in Eq. (2), derived by experimental observation, with Eq. (3), it is obvious to draw the conclusions reported in relationships (4).

$$pur_{DX}^{P} = f(Jv, pur_{DX}^{F1}),\ pur_{DX}^{R1} = f(Jv, pur_{DX}^{F1}) \tag{4}$$

The whole experimentation is documented in the following sections by using this procedure for data reduction.

3.2. Modules KOCH-4720SR2-N1 and GE-DK4040C1027

Modules K-SR2 and GE-DK were tested according to the following plant configuration; the corresponding experimental procedure is also specified.

Plant configuration: (a) (Fig. 2)-total recirculation mode of Retentate, in which P is continuously withdrawn out of the plant whereas R1 is fed back to the tank; concentrations of all streams are time-dependent.
Controlled quantities: temperature and pressure in F1, pH in the tank, DS wt% and DX purity at the initial condition in the tank.
Measured quantities: $\omega_{DS}^{F1}, pur_{DX}^{F1}, \omega_{DS}^{R1}, pur_{DX}^{R1}, \omega_{DS}^{P}, pur_{DX}^{P}, Q_P, Q_{R1}$ as a function of time.

The compositions of DX and impurities in all the streams can be calculated straightforwardly, as well as the total flux and all the quantities defined in Eqs. (1) and (2). Results are reported in Figs. 3 and 4, for all the trials performed; experiments were carried out at different initial DS wt% values in the tank.

3.3. Module KOCH-MPS34A2Z

Module K-MPS34 was tested according to the following plant configuration; the corresponding experimental procedure is also specified.

Plant configuration: (b) (Fig. 2)-partial recirculation mode of Retentate, in which P is continuously withdrawn out of the plant whereas R is fed back to the tank; concentrations of all streams are time-dependent.
Controlled quantities: temperature and pressure in F1, Q_{F1}, pH in the tank, DS wt% and DX purity at the initial condition in the tank.
Measured quantities: $\omega_{DS}^{F}, pur_{DX}^{F}, \omega_{DS}^{R}, pur_{DX}^{R}, \omega_{DS}^{P}, pur_{DX}^{P}, Q_P, Q_R$ as a function of time.

Mass balances can be used to calculate flow rates and compositions of all the streams, including $Q_{RR}, Q_{R1}, \omega_{DS}^{F1}, pur_{DX}^{F1}$ as a function of time. Finally, the compositions of DX and impurities in all the streams can be obtained straightforwardly, as well as the total flux and all the other quantities defined in Eqs. (1) and (2). Results are reported in Fig. 5, for all the trials performed; experiments were carried out at different initial DS wt% values in the tank and at two feed flow rates. It can be observed that neither total flux nor rejections are sensitive to the feed flow rate in the range investigated.

3.4. Module GE-DL4040C1025

3.4.1. The role of feed flow rate (Q_{F1})

Experiments with plant configuration (b) (Fig. 2), in total recirculation mode of Permeate, were performed in order to investigate

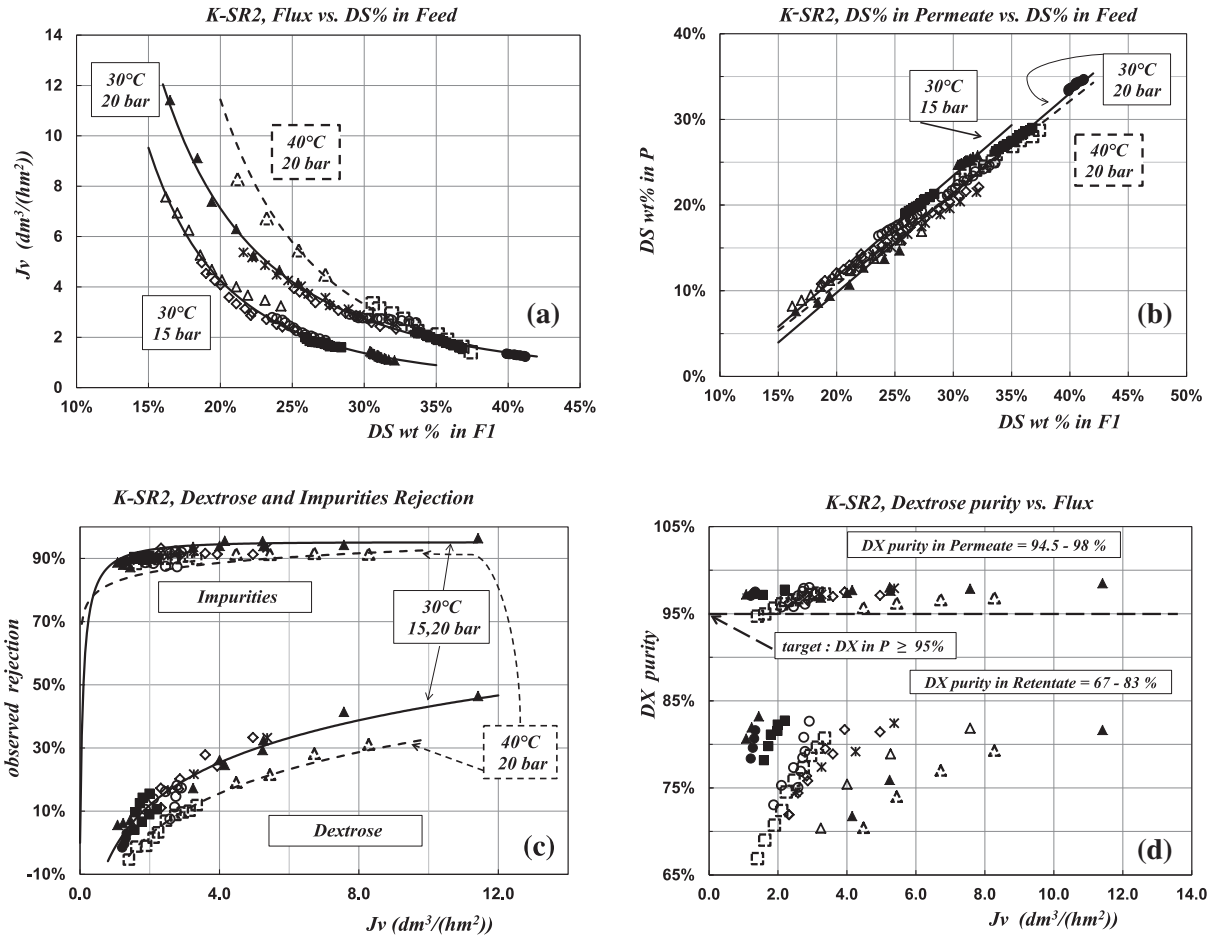


Fig. 3. Module KOCH 4720SR2-N1. NF of real solutions in plant configuration (a) (Fig. 2): pH = 3.8–4.5, QF1 = 1380 dm^3/h, initial DX purity in tank = 80–83%; pressure and temperature are measured at the inlet section of the module; "dashed" data are experiments at 40 °C; different symbols correspond to different trials. (a) Total volume flux vs. DS wt% in the feed; (b) DS% in Permeate as a function of DS% in the feed; (c) observed rejection of DX and IMP vs. total flux; (d) DX purity in Permeate and in Retentate vs. total flux.

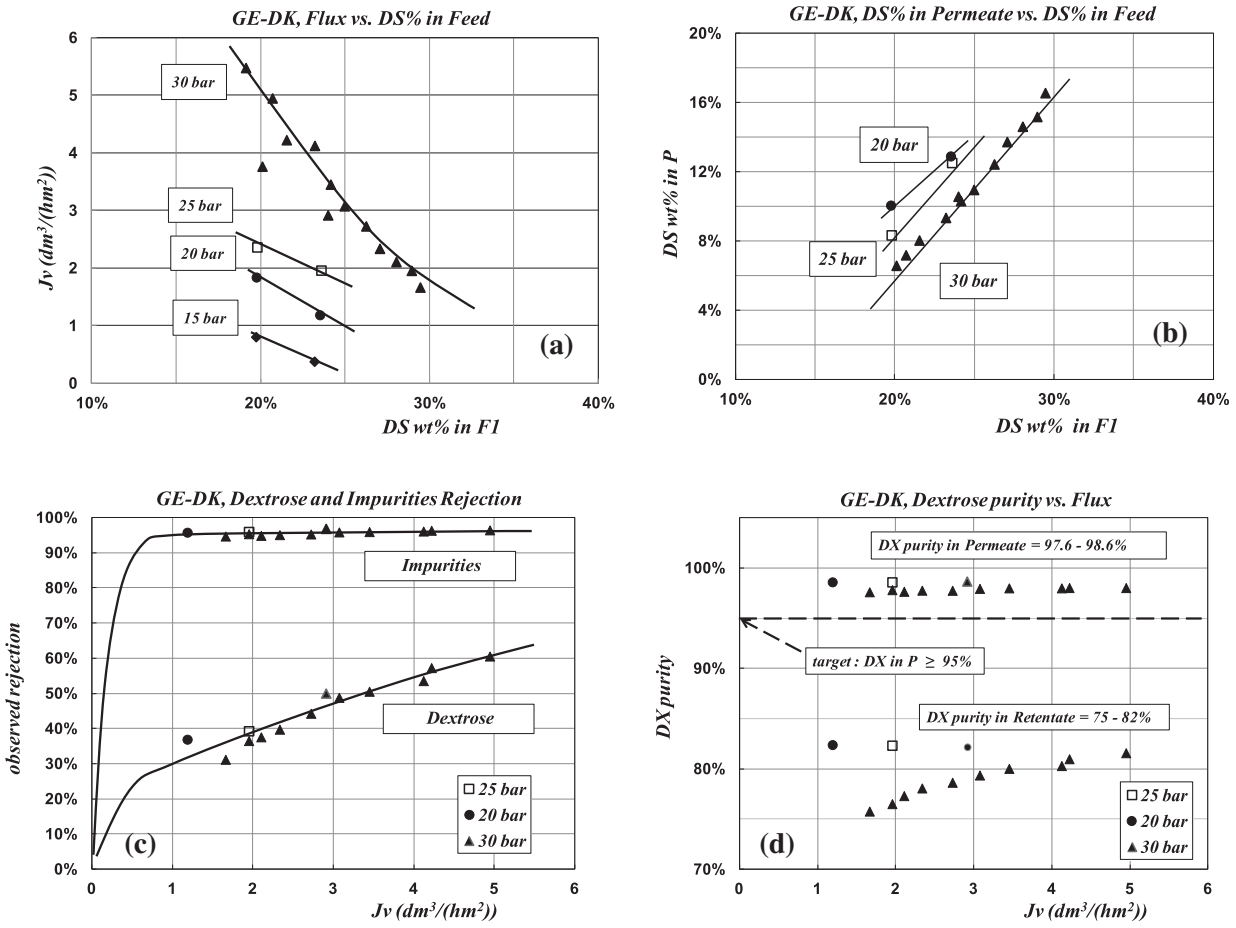


Fig. 4. Module GE DK 4040 C1027. NF of real solutions at 50 °C in plant configuration (a) (Fig. 2): pH = 4, QF1 = 1380 dm^3/h, initial DX purity in tank = 82–83%; pressure is measured at the inlet section of the module; different symbols correspond to different trials. (a) Total volume flux vs. DS wt% in the feed; (b) DS% in Permeate as a function of DS% in the feed; (c) observed rejection of DX and IMP vs. total flux; d) DX purity in Permeate and in Retentate vs. total flux.

the role of feed flow rate at the inlet section of the module GE-DL; effects are investigated on total flux and on the pressure drops across the module. It was observed that the best operative conditions at 50 °C were located in the range from 2300 to 3500 L/h: in that range, no sensible variation in total flux was measured, and, correspondingly, low pressure drops per module were obtained, lower than 0.4 bar at 50 °C.

3.4.2. Module performances

Experiments were performed according to the same procedure as for module KOCH-MPS34A2Z as well as to the same procedure for data elaboration. Results are reported in Fig. 6, for all the trials performed; experiments were carried out at different initial DS wt% values in the tank.

3.4.3. Long time trials

Fouling was investigated in GE-DL module, by performing two experiments, 9 and 15 h long, respectively.

Plant configuration: (b) (Fig. 2) in total recirculation mode of Permeate.
Controlled quantities: temperature and pressure in F1, Q_{F1}, pH in the tank, DS wt% and DX purity at the initial condition in the tank.
Measured quantities: $\omega^F_{DS}, \omega^P_{DS}, Q_P$ as a function of time.

Results are reported in Fig. 7. Apparently, there is a flux decrease as a function of time, due to the membrane fouling, with respect to the values measured with a clean module at the initial condition; in both cases, the flux decrease is stabilized to 70% of the initial values after 6–8 h and approaches a constant value after 12 h. However, the higher decrease in total flux is observed in the first hour, which is close to 20%. During experimentation, no variations in DS content was measured in the Permeate nor in the Retentate, thus showing that separation efficiency is not affected by fouling.

3.5. Discussion

A lot of experimental data are available, and some interesting general conclusions can be drawn.

All the modules tested show remarkable analogies in their behavior as a function of operative conditions.

Basically, the effect of pressure and temperature on flux and rejection is quite typical of Nanofiltration processes: flux increases with pressure and temperature, rejection decreases as the temperature increases.

A general trend is observed in which module performances can be described by using few simple quantities (as introduced in Section 3.1), in a wide range of confidence, in spite of the complexity of the solutions investigated. For all the modules tested, at a given pressure value, total volume flux as well as DS wt% in Permeate depend mainly on DS wt% in the feed and they are independent of the feed/Retentate purity, which varied in the range from 67% to 83% (see Figs. 3–6, cases (a), (b) and (d)).

Observed rejections of DX and Impurities are mainly dependent on total volume flux, according to the typical trend generally obtained in pressure driven processes of neutral solutes (see

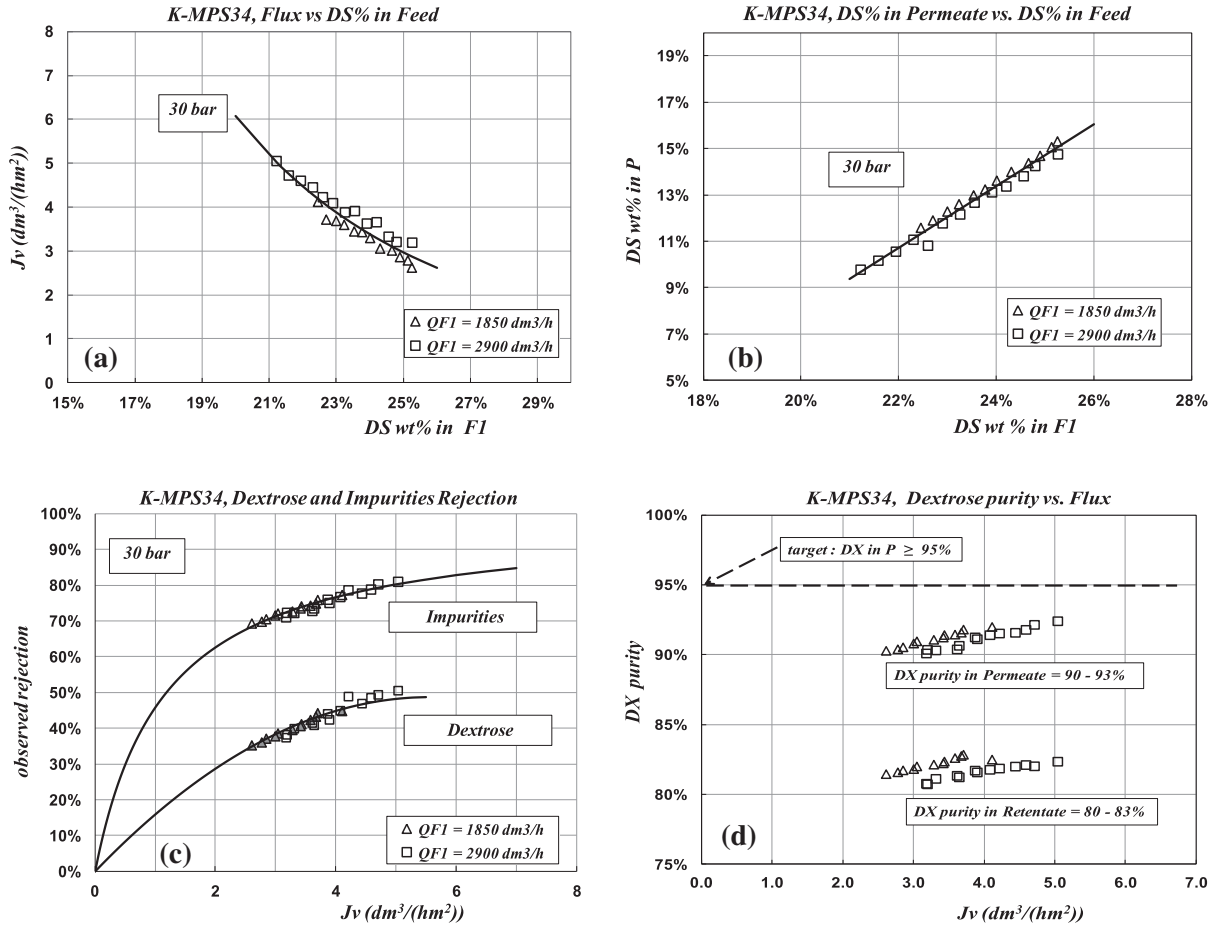


Fig. 5. Module KOCH MPS-34A2Z. NF of real solutions at 50 °C in plant configuration (b) (Fig. 2): pH = 4, initial DX purity in tank = 83%; pressure is measured at the inlet section of the module; different symbols correspond to different trials. (a) Total volume flux vs. DS wt% in the feed; (b) DS% in Permeate as a function of DS% in the feed; (c) observed rejection of DX and IMP vs. total flux; (d) DX purity in Permeate and in Retentate vs. total flux.

Figs. 3–6, case (c)). This should not be a surprise, in passing we can remind that this behavior is predicted also by the well-known solution–diffusion model or similar models [37].

Those results are very interesting, if they are considered altogether. In this paper we are focused on modules characterization in order to obtain information useful for the process design and scale-up. The analogies observed in the performances of each module put clearly in evidence that only few well-defined experiments are sufficient to draw conclusions about the process feasibility with the module under investigation. In other words, the experimental procedure here introduced, together with the criterion developed for data reduction, gives a general indication about the experimentation protocol to be performed in order to obtain basic data; experiments as a function of time in which DS content increases give overall information about fluxes and DS% in the Permeate, whereas further analyses of some samples of Permeate and Retentate can show the separation efficiency of the module. We can observe that only two experimental runs were performed to conclude about the applicability of module KOCH-MPS34A2Z (Fig. 5).

Notwithstanding module performances are quite similar in their general behavior, the values of the relevant parameters are remarkably different and only one kind among the modules tested fits the requirements for the industrial application of this project. The best module should allow a DX purity in the Permeate greater than 95%, in correspondence with transmembrane fluxes not lower than 4 $dm^3/(hm^2)$ and a DS content in the Permeate possibly higher than 15% in order to reduce costs in the evaporation steps downstream the NF process.

As a consequence, modules KOCH-MPS34A2Z and GE-DK4040C1027 are to be rejected. The former does not allow to achieve the DX purity in the Permeate (which is lower than 93%, Fig. 5d)), whereas the latter gives too low fluxes. Basing on data in Fig. 4, at 30 bar, the value of 15 wt% DS in Permeate can be obtained at 29 wt% DS in F1, which corresponds to a value of 2 $dm^3/(hm^2)$ volume flux. That value is to be considered as too low for industrial application, since during operation it certainly undergoes a remarkable decrease owing to membrane fouling.

On the other hand, module KOCH-4720SR2-N1 fulfills the DX purity in the Permeate at 30 °C, whereas at 40 °C the requirement is not fulfilled in all the composition range. At 30 °C, the value of 15 wt% DS in Permeate can be obtained operating at 20 bar at 25 wt% DS in F1, which corresponds to a value of 4 $dm^3/(hm^2)$ volume flux. Although that value of flux is not to be rejected, 30 °C operating temperature is not optimal for sugars solutions, since it greatly enhances fermentation processes.

Finally, module GE-DL4040C1025 represents the better compromise among DX purity, DS wt% in Permeate and transmembrane flux. First of all, the module can work at 50 °C which is a very good temperature for fermentation inhibition; secondly, at 50 °C DX purity in the Permeate is greater than 97.5% in all the composition range investigated. Furthermore, at 30 bar, the value of 15 wt% DS in Permeate can be obtained operating at 28 wt% DS in F1, which corresponds to a value of 9 $dm^3/(hm^2)$ volume flux. In addition, operating at 30 bar and 50 °C, values of flux close to 6 $dm^3/(hm^2)$ are obtained in correspondence of 35 wt% DS in F1; that means that the NF step can operate at high DS compositions

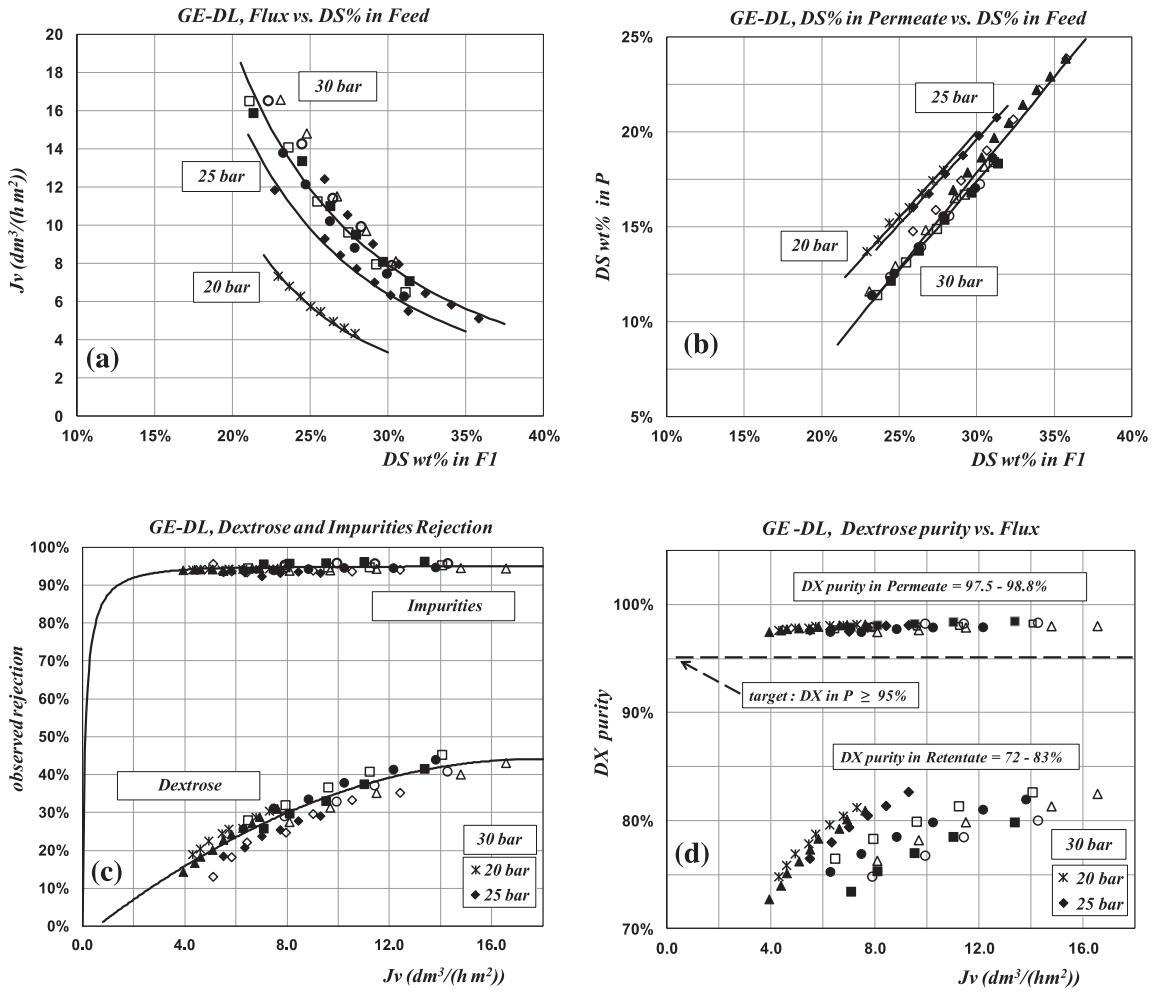


Fig. 6. Module GE DL4040C1025. NF of real solutions at 50 °C in plant configuration (b) (Fig. 2): pH = 3.8–4.5, QF1 = 2300–3500 dm^3/h, initial DX purity in tank = 81–83%; pressure is measured at the inlet section of the module; different symbols correspond to different trials. (a) Total volume flux vs. DS wt% in the feed; (b) DS% in Permeate as a function of DS% in the feed; (c) observed rejection of DX and IMP vs. total flux; (d) DX purity in Permeate and in Retentate vs. total flux.

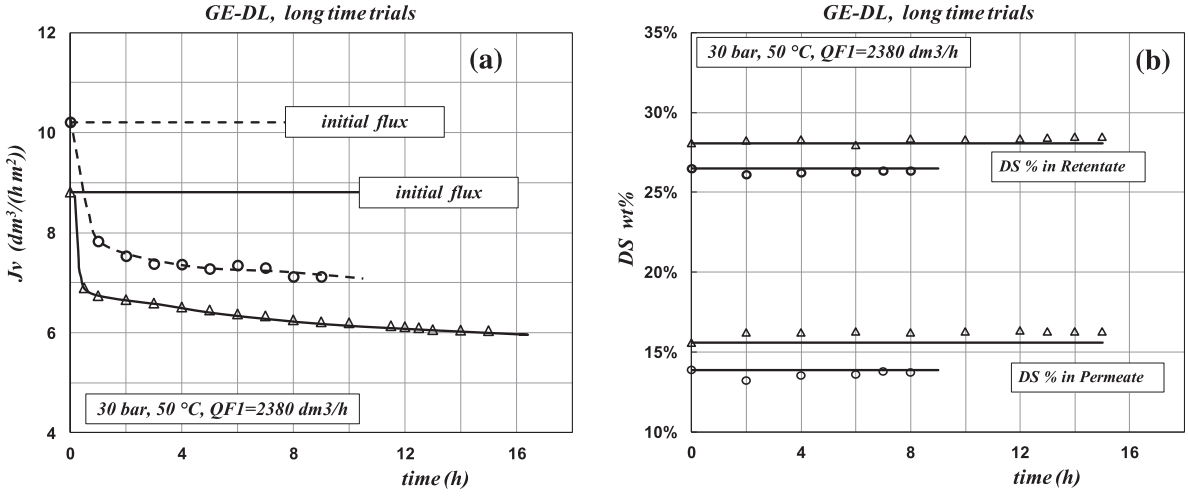


Fig. 7. Module GE DL4040C1025: long time trials. NF of real solutions at 50 °C in plant configuration (b) (Fig. 2) in total recirculation mode of Permeate: pH = 4.5, QF1 = 2380 dm^3/h, DX purity in tank = 81%; pressure is measured at the inlet section of the module. (a) Total volume flux vs. time; (b) DS% in Permeate and in Retentate vs. time.

also, thus decreasing dilution of the mother liquor which originally contains total DS in the range from 45 to 55 wt%.

In summary, modules GE-DL can fulfill the requirements, working in a wide range of operative conditions: at 50 °C and 30 bar, in a range of feed flow rates from 2300 to 3600 dm^3/h, DX purity in the Permeate can be always obtained greater than 97%; correspondingly, the NF plant can be designed to work with a DS content in F1 from 22 wt% to 35 wt%, obtaining a total fluxes from 16 to

6 $dm^3/(hm^2)$ and a DS content in the Permeate from 11.5 wt% to 22.5 wt%, correspondingly.

Finally, accounting for the long time trials results (Fig. 7), it can be also concluded that purities and DS compositions obtained with the cleaned membrane can be expected to be realistic values, whereas a Clean-In-Place procedure should be defined in order to reduce the fouling problems as much as possible.

As a conclusive discussion, some comments are in order, about GE modules in comparison with KOCH modules.

Basing on data reported in the technical sheets, GE-DK and GE-DL modules should give similar results: in view of a slightly higher hydraulic permeability, module DL should deliver slightly higher fluxes than module DK, and, correspondingly with the $MgSO_4$ retentions, slightly lower dextrose rejections should be expected for DL module. For those membranes, pore radius and effective thickness estimated by conventional steric models are quite similar [38–41]. In addition, since all the experiments were performed with solutions coming from a demineralization step, at pH close to 4, which corresponds to the isoelectric point of the membrane [42–44], membrane charge effects can be certainly assumed as negligible. Results reported in Figs. 4 and 6 give therefore a confirmation of the expectation, although experimental fluxes with DK module are remarkably lower than DL, and, correspondingly, the observed rejections of dextrose are higher. Those differences can be only ascribed to differences related to the module geometry; DK and DL modules are assembled with different feed spacers, 30 mil and 50 mil, respectively. Experience shows [45] that thin spacers can give more compaction problems than wider spacers, thus leading to a permeability decrease; in passing, also manufacturers suggest wider spacers in high temperature operations. In addition, although DL module operated at feed flow rates from 2300 to 3500 dm^3/h, corresponding to effective velocities in the range from 0.19 to 0.30 m/s, remarkably higher than the feed flow rate in DK module of 1380 dm^3/h, corresponding to an effective velocity of 0.13 m/s, the effect of concentration polarization in DL modules can be suspected to be increased by the higher fluxes.

With regards to KOCH modules, analogous considerations can be drawn. In particular, since K-SR2 membrane is much more permeable than K-MPS34, lower dextrose rejections are observed, decreasing to negative values at very low fluxes. Unfortunately, that phenomenon occurs at too low fluxes to have an industrial interest.

4. Conclusions

A wide experimentation was carried out to test performances of industrial NF modules for Dextrose (DX) recovery from crystallization mother liquors.

Four commercial industrial spiral wound modules with polyamide membranes were tested to obtain information about the DX purity and the total Dry Substance (DS) in the Permeate, as well as about total volume fluxes. Tests were carried out by using industrial real solutions at different dilutions with demi-water, in a wide range of DS composition in the Feed.

The following conclusions are in order.

1. All the modules tested show a quite similar behavior, which can be described by using few simple quantities (DS wt% in feed, DS wt% in Permeate, DX purity, total flux, DX rejection and Impurities Rejection), in spite of the complexity of the solutions investigated. It is generally sufficient to perform only few well-defined experiments in order to obtain data useful for process design and scale-up.
2. Nanofiltration is a feasible technique to achieve Dextrose enrichment of mother liquors from crystallization step.
3. Modules tested show very different process efficiencies; only the module GE-DL4040C1025 fits the industrial requirements for the application of the process. It can be used at 50 °C and 30 bar, in a range of feed flow rates from 2300 to 3600 dm^3/h, thus obtaining DX purity in the Permeate always greater than 97%; correspondingly, the NF plant can be designed to work with a DS content in the feed from 22 wt% to 35 wt%, obtaining a total fluxes from 16 to 6 $dm^3/(hm^2)$ and a DS content in the Permeate from 11.5 wt% to 22.5 wt%, correspondingly.
4. Data reported in this paper are the basis to design the Nanofiltration plant: they can be used to calculate the average total flux and then the minimum value of the total membrane area required for a given plant specification, and finally to define both the plant configuration and the corresponding module arrangement. The problem is going to be developed in a following paper.

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